

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

**(19) World Intellectual Property
Organization
International Bureau**



(43) International Publication Date
19 February 2004 (19.02.2004)

PCT

(10) International Publication Number
WO 2004/015252 A1

(51) International Patent Classification⁷: F01N 3/023,
3/022, 3/08, 3/031, 3/20

(74) Agent: NUNN, Andrew, Dominic; Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading RG4 9NH (GB).

(21) International Application Number:
PCT/GB2003/003462

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(22) International Filing Date: 8 August 2003 (08.08.2003)

(25) Filing Language: English

(26) **Publication Language:** English

(30) Priority Data:
0218540.3 9 August 2002 (09.08.2002) GB

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(71) **Applicant (for all designated States except US): JOHN-
SON MATTHEY PUBLIC LIMITED COMPANY**
[GB/GB]; 2-4 Cockspur Street, Trafalgar Street, London
SW1Y 5BO (GB).

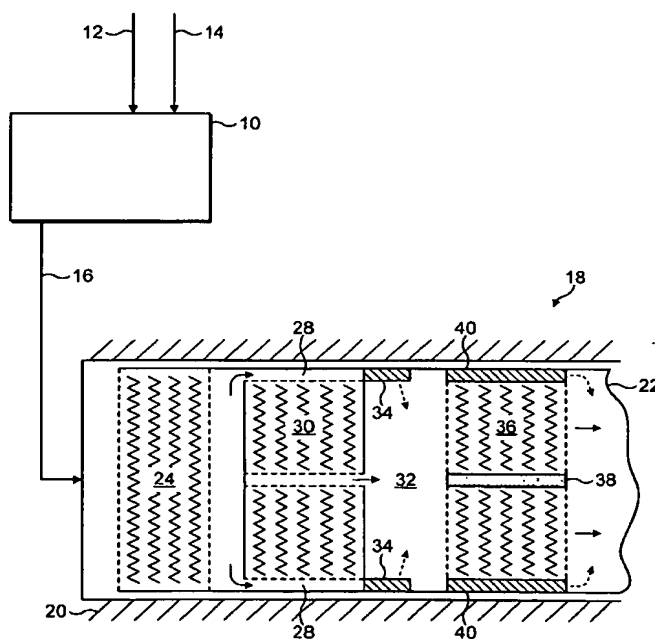
Published:
— *with international search report*

(72) Inventor; and

(75) **Inventor/Applicant (for US only): TWIGG, Martyn, Vincent [GB/GB]; 108 Ermine Street, Caxton, Cambridge CB3 8PO (GB).**

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: EXHAUST SYSTEM FOR A LEAN-BURN IC ENGINE



(57) Abstract: An exhaust system for a lean-burn internal combustion engine comprises a filter (30, 36) for particulate matter and means (24) for generating an oxidant more active than molecular oxygen for combusting particulate matter disposed on the filter (30, 36), wherein the filter (30, 36) comprises a mass of elongate flat, narrow strip metal.

WO 2004/015252 A1

EXHAUST SYSTEM FOR A LEAN-BURN IC ENGINE

The present invention relates to an exhaust system for a lean-burn internal combustion engine, and in particular to a system for treating a soot-containing gas.

Whereas filtering soot from engine exhaust gas by ceramic wall-flow filters has become well established, use of metal-based filters is less so. Metal-based filters were disclosed *inter alia* in US-A-4,270,936 and US-A-4,902,487 and in SAE papers 820184 (Enga et al.) and 890404 (Cooper, Thoss). They reached an advanced stage of development in Johnson Matthey's 'Catalytic Trap Oxidiser' ('CTO'), but appear not to have successfully competed with wall-flow filters in the commercial market. We have recently identified systems in which metal-based filters can be used with advantage.

According to the invention there is provided an exhaust system for a lean-burn internal combustion engine, which engine comprising an exhaust gas treatment system comprising a soot filter packed with a mass of elongate flat, narrow strip metal and means for generating an oxidant more active than molecular oxygen (O_2) for combusting soot collected on the filter.

By "elongate" herein, we mean relative to the width of the flat of the flat strip metal. The term "narrow" is to be interpreted accordingly.

By "packed" herein, we also mean "compacted" and "compressed".

The exhaust gas from such an engine typically contains the gaseous components soot (or particulate matter (PM)) unburned hydrocarbons (HC), carbon monoxide (CO), nitrogen oxides (NO_x), carbon dioxide (CO_2), water vapour (H_2O), O_2 and nitrogen (N_2). The means to remove by combustion the soot collected on the filter preferably operates continuously. The oxidant more active than O_2 is for example ozone and/or plasma, most conveniently NO_2 . Such NO_2 is preferably provided, at least in part, by catalytic oxidation of the NO component of the NO_x e.g. on a NO-oxidation catalyst e.g. platinum supported on particulate alumina upstream of the filter. Such catalyst

may be supported on a packed flat, narrow strip metal substrate, conveniently of the type used in the filter, but at a lower packing density, to permit passage of soot particles.

Alternatively or additionally the filter packing may carry a layer catalytic for soot oxidation, possibly by a mechanism involving oxidation of NO to NO₂. Such soot oxidation catalysts include supported platinum group metals, such as platinum on alumina and/or base metals such as La/Cs/V₂O₅. If the engine-out NO_x available in the gas is insufficient to combust the soot continuously, more may be introduced, e.g. by introduction of plasma or NO_x or nitric acid, possibly as gas produced by oxidation of ammonia on-vehicle.

The ozone and/or plasma may be generated by suitable means such as a source of UV light and/or a corona discharge device. It is to be understood that plasma and/or ozone is capable of oxidising NO to NO₂. In one embodiment, the exhaust system comprises both means for generating ozone and/or plasma and as NO oxidation catalyst.

The external structure of the filter may have features providing operational advantages. For example, it may be formed as a monolith easily inserted into or withdrawn from a reactor shell. Whether monolithic or not, it may be disposed as a cartridge in an outer shell, easily insertable or withdrawable. It may be capable of electrical conduction as a whole, thus permitting electric heating at cold start. Such electrical conduction may be used in constructing a monolith, by effecting local welding between adjacent strips; if the filter is to be disposed in an outer shell. It may contain an axial metal rod to act during such welding as one electrode, the shell acting as the other. Further external features are mentioned below.

The metal of the filter should be capable of withstanding the exhaust treatment process conditions. Since the filter can be replaceable more easily than a ceramic filter, and its material can be recovered for re-use, the use-life of the filter need not be as long as for a ceramic filter. It is possible to envisage replacing the filter at the normal service interval of a vehicle.

Typically the metal is a corrosion resistant iron alloy. Typical alloys contain nickel and chromium and minor constituents as in Type 300 or Type 400 stainless steels. Which is used may depend on whether the exhaust gas treatment system is required to operate temporarily in rich conditions, in which some stainless steels are unstable. For a wide variety of exhaust compositions a preferred iron alloy contains at least 11.5% Cr, 4% Al and 0.02-0.25% minor constituents such as rare earth, zirconium or hafnium. The metal in a filter may be a mixture of different compositions, possibly including a component providing electrical conduction bridges or a welding function.

The filter may have, wholly or domain-wise, a regular structure, for example coiled, woven or knitted. The metal strip of the filter may be for example up to 2, especially in the range 0.1 to 0.5mm, wide. It should be thick enough to afford mechanical strength in the conditions in which it is to be used. Typically its thickness is in the range 0.2 to 0.8 of its width. Suitably its geometric surface area per unit length is in the range 1.2 to 1.5 times that of the same weight of metal in circular cross-section. It is suitably the product of flattening circular-section wire. The metal in a filter unit may be a mixture of strip dimensions and may include circular-section wire as unflattened interlengths or as added sub-units. In one embodiment, the flat narrow, strip metal is of flattened wire.

The level of packing can be chosen to provide a desired level of filtration and/or backpressure in the system, and can depend on the width and depth of the flat metal strip. However, we believe that generally a range of packing density of from 2.5 to 30% v/v, such as 5 to 15% v/v can provide the desired result. We have used a packing density of 10% with advantage.

A catalytic coating on the filter typically comprises a washcoat of oxide such as alumina with possibly rare earth and an active material especially Pt or Pd or oxides of Cs and V. The coating may contain perovskite. If catalytic oxidation of NO is used, the catalyst typically comprises Pt and/or Pd on such a washcoat. If ozone is used, the generator thereof may be for example a corona discharge tube through which air passes between two electrodes kept at a large potential difference; or may comprise a high-

energy lamp. If plasma is used, the plasma generator may operate for example by corona discharge, surface plasma discharge or dielectric barrier discharge or comprise a dielectric packed bed or electron beam reactor. It may be enhanced by electromagnetic radiation such as microwave radiation. The generator may treat air or the whole of the exhaust gas or part of such gas before or after treatment.

The size of the filter(s) relative to the engine and any arrangements to introduce additional oxidant more active than O_2 may be the subject of design features. In the simplest case filter capacity is large enough so that soot is combusted continuously by the oxidant, that is, with any accumulation during slow running being quickly removed in periods of fast running; the overall trend being continuous combustion. A less expensive filter capacity is sized to accommodate larger accumulations of soot, sufficient to increase pressure-drop significantly before the next period of fast running. Such filter(s) preferably includes a bypass, the pressure-drop through which is equal to the design maximum tolerated pressure-drop. The bypass avoids engine stalling or low power that would result from excessive pressure-drop, but permits some soot emission to atmosphere. To cope with such soot emission a second stage such as a filter or impingement collector and/or an oxidation catalyst may be provided downstream of the bypass. The bypass, without or with second stage filter and/or oxidation catalyst, may be part of the filter cartridge.

The direction of gas flow through the filter and/or (if used) oxidation catalyst can be or have a component linear or transverse to the general flow direction. Transverse flow may be for example symmetrical, especially inwards to an outflow header axial in a cylindrical filter, or to a plenum in an oval-section or rectangular filter. Alternatively one-way cross-flow may be provided.

In a further elaboration of the process and system a succession of filter elements presents to the gas a different soot-treating capacity, for example collecting smaller and smaller particles, and/or providing graded catalytic environments. Preferably gas flow in the filter element(s) at the inlet of the succession is, or has a component, transverse to the general direction of flow. If the process and system includes subjecting soot to oxidant more active than molecular oxygen, successive filter elements may alternate

with oxidation catalyst and/or with means to provide plasma or ozone. In such succession downstream filter element(s) and (if used) oxidation catalyst(s) may be ceramic.

A particularly useful system comprises, in downstreamward order, a plurality of metal-based filters for successively trapping smaller and smaller particles and , optionally, at least one wall-flow filter for trapping yet smaller particles. In this system the pores of the wall-flow filter can be smaller than in single-stage wall-flow trapping, because the preceding metal-based filters have removed the larger particles that may have blinded or blocked, i.e. reduced the gas flow through, them. Any or all of the filters may be catalysed.

Instead or in addition a distinct NO-oxidation catalyst may be disposed upstream of at least the first filter. Such catalysis on and/or between filters can have the effect of restoring the NO₂ content, which may have had been decreased by reaction with soot in the preceding filter. The filters and, if present, catalysts, may be assembled as a single unit within a cartridge. Such NO-oxidation catalysts can be supported on a flow through substrate e.g. a ceramic or metal substrate.

According to a further aspect, the invention provides a system according to the invention wherein the oxidant more active than O₂ is at least one of ozone, plasma or NO₂.

The exhaust treatment system may include other integers as used or proposed, for example a three-way catalyst (TWC), nitrogen oxide (NO_x) trap + regeneration means, selective catalytic reduction (SCR) e.g. using hydrocarbon or ammonia as reductant, lean-NO_x catalysis, a sulfur oxides (SO_x) trap regenerable or disposable. The engine and system may include control gear, in use, for controlling the operation of the exhaust system to reduce emissions and on-board diagnosis gear as usual or adapted to novel features of the invention.

The lean-burn engine may be any engine currently or potentially producing a soot-containing engine. For example the engine may be a compression ignition engine, such as diesel engine, or a spark ignition engine such as a lean burn gasoline, e.g. gasoline direct injection (GDITM), engine. It may have exhaust gas recirculation (EGR). It may be for light or heavy duty. To provide for the low SO₂ content of the exhaust gas, the S content of the fuel used should be less than 500, especially less than 50ppm w/w as S. Low sulfur fuelling and lubrication giving exhaust gas of less than 20ppm SO₂ is preferred.

In order that the invention may be more fully understood embodiments whereof will be described with reference to the accompanying drawings and by reference to the illustrative Example, wherein:

Figure 1 shows in schematic section a diesel engine with an exhaust system;

Figure 2 is a trace showing exhaust gas aftertreatment component inlet temperature and outlet temperature in the exhaust system of a vehicle against time, also showing vehicle speed;

Figure 3 is a schematic sectional view through an exhaust gas treatment system component for use in the present invention;

Figure 4 is a bar chart showing particulate mass measured over a drive cycle for exhaust gas treatment systems 1, 2 and 3; and

Figure 5 shows modal (second by second continuous) analysis of tailpipe NO₂ from an exhaust system comprising systems 1, 2 and 3.

Referring to Figure 1, item 10 indicates a 4-cylinder diesel engine having air inlet 12 and fuel inlet 14 fed with hydrocarbon of 5 ppm sulfur content at an air/fuel weight ratio of about 30 for steady operation but variable as routinely practised. The engine exhaust 16 is fed to a cylindrical treatment reactor indicated generally by 18 and having insulated internal walls 20. Fitting snugly within walls 20 is filter cartridge 22.

At the inlet end of cartridge 22 and occupying its whole diameter is catalyst bed 24, packed with knitted 310 stainless steel flattened wire 0.33mm wide and 0.2mm thick to 6% solid by volume, carrying an alumina washcoat and Pt at 70-100 ($1.98 - 2.83 \text{ gm}^{-3}$), possibly up to 300 (8.50 gm^{-3}), g/ft^3 of bed volume, giving low-temperature light-off. The next downstream zone of cartridge 22 is occupied by annular feed channel 28 surrounding first filter 30 packed with the same flattened wire as in bed 24 but at 12% volume by volume and carrying a washcoat and soot oxidation catalyst. Filter 30 provides axial-inward gas flow to outlet 32. Feed channel 28 terminates longitudinally in bypass 34, the function of which will be explained below. The next downstream zone is second filter 36, providing longitudinal gas flow. Axial to filter 36 is metal rod 38, the function of which is to be explained below. Filter 36 is packed with the same flattened wire as used in bed 24 but at 16% volume by volume and carrying a soot oxidation catalyst e.g. $\text{La/Cs/V}_2\text{O}_5$. Filter 30 and/or 36 may be rigidified, at the time of construction, by electric internal spot welding using respectively the axial outlet or axial rod 38 as one electrode and the outer boundary member as the other electrode. Surrounding filter 36 is bypass channel 40. Bypasses 34 and 40 are shown shaded to indicate the possible inclusion of flow-obstructing material to provide balancing of pressure-drop with that of the filter when the filter is partly soot-bearing. Instead of or in addition to the soot oxidation catalyst on filter 36, there may be a second oxidation catalyst, similar to 24, between the filters.

In operation, NO in the exhaust gas entering bed 24 is largely oxidised to NO_2 . Soot in the gas passes through bed 24 and is held on filter 30 where it is oxidised by the NO_2 to CO. If filter 30 is under-designed or an engine upset produces extra soot, soot accumulates in it and obstructs gas flow through it. At a design, i.e. pre-determined, level of pressure-drop due to such obstruction, bypass 34 permits gas to pass through the exhaust system, so that engine operation can continue until soot-oxidising conditions return or remedial action is taken. Likewise, if soot accumulates in filter 36 to a design level, bypass channel 40 permits gas to pass.

Filters as 30 and 36, and possibly others in succession, provide successively increasing geometric surface per unit volume, to trap finer particles or bypassed particles. Such successive filters need not include a bypass, if the entering

concentration of soot is sufficiently less than in the first filtering stage. Such further stage(s) may include oxidation catalyst as mentioned above to restore the content of NO_2 following reduction by soot on the preceding filter.

Example

A 2.5 litre Audi TDI vehicle certified for European Stage 2 legislative requirements, and fuelled with 50ppm sulphur containing diesel fuel, was fitted with a flow through ceramic monolith 5.66in (144mm) diameter and 9in (225mm) long with a cell density of 400 cells per square inch (cpsi) (62 cells cm^{-2}) and 6mil (thousandths of an inch) (0.15mm) wall thickness. The vehicle was placed on a standard chassis rolling road dynamometer and, after 20 seconds idling was accelerated to 120kph in 100 seconds and maintained at this speed for the remainder of the test. After a further 300-400 seconds the inlet temperature to the catalyst system attained a stable temperature of $330\text{-}350^\circ\text{C}$. The vehicle was then run for a period of 20 minutes at this temperature (Figure 2). During the 20 minute period particulate was collected on two sets of filter papers by the standard method (one set for each 10 minute period) to enable an average particulate weight for the test to be calculated. During the same 20 minute period Nitrogen Oxides (NO and NO_2) were measured in the feed gas to the monolith, and the tail pipe gas after the monolith by chemiluminescent analysis and Fourier Transform Infra Red (FTIR) respectively. This was labelled System 1.

The flow through monolith was removed from the vehicle and replaced by a 5.66in (144mm) diameter and 4in (100mm) long flow through monolith of the same cell density and wall thickness coated with a platinum catalyst at 75g ft^{-3} (2.6g litre^{-1}) followed by a bare flow through monolith 5.66in (144mm) diameter and 4in (100mm) long. The identical test cycle was conducted and the measurements repeated. This was labelled System 2.

The oxidation catalyst was replaced by one 5.66 (144mm) diameter and 3in (76mm) long flow through monolith coated with platinum at 75g ft^{-3} (2.6g litre^{-1}), and the bare monolith was replaced by a particulate trap of novel design. This consisted of

a packed bed of knitted, stainless steel flattened wire, 0.10mm wide and 0.05mm thick, occupying the whole diameter of the rear face of the catalyst and abutting against it. The total length of the wire bed was 4in (100mm) and the packing density was 10% v/v. This was followed by a 5.66in (144mm) diameter and 1in (25.4mm) long flow through monolith coated with platinum at 75g ft^{-3} (2.6g litre^{-1}) ("catalyst slice") abutted against the rear face of the knitted wire substrate. This catalyst was followed in turn by a second knitted wire substrate and a bare monolith, having the same dimensions as the preceding first knitted wire substrate and catalyst slice. The arrangement is shown in Figure 3. Therefore the total volume and aspect ratio of catalysed flow through monolith was the same as that of System 2. This last system was labelled System 3. The identical drive cycle and measurements were repeated as for Systems 1 and 2.

Figure 4 summarises the particulate mass measured over the drive cycle for the three systems. Thus a lowering of particulate from the "baseline" System 1 by the addition of oxidation catalyst is obtained in System 2 and a further improvement with the addition of the packed wire bed which retains a proportion of the soot allowing NO_2 exiting the first catalyst, to react with it. It can be seen that the conversion efficiency of System 2 relative to system 1 is 13%, whereas the conversion efficiency of System 3 relative to System 1 is 38%.

Figure 5 shows modal (second by second continuous) analysis of NO_2 at the tailpipe downstream of the three systems. System 1, with a bare monolith has very low NO_2 emissions similar to those from the engine. Higher NO_2 concentrations are measured after System 2 because NO is oxidised over the catalyst, but there is only a small amount of reaction with soot. In System 3 NO_2 formed over the first oxidation catalyst reacts with soot collected in the first filter bed. The NO not oxidised over the first catalyst passes through the first filter bed and is oxidised to NO_2 over the second catalyst. There may also be some re-oxidation of NO formed from reaction between $\text{NO}_2 + \text{C} \rightarrow \text{NO} + \text{CO}$. This NO_2 together with any NO_2 not reacted in the first filter reacts with soot collected in the second filter bed resulting in lower soot and NO_2 tailpipe levels, compared to System 2. Turbulent flow, initiated in the gas stream by its

passage through the filter bed, enhances the reactions of NO_2 with the soot and the oxidation of NO over the second catalyst.

CLAIMS:

1. An exhaust system for a lean-burn internal combustion engine comprising a soot filter packed with a mass of elongate flat, narrow strip metal and means for generating an oxidant more active than molecular oxygen (O_2) for combusting soot collected on the filter.
2. A system according to claim 1, wherein the oxidant more active than O_2 is at least one of ozone, plasma or NO_2 .
3. A system according to claim 2, wherein the NO_2 is provided, at least in part, by catalytic oxidation of the NO component of the NO_x contained in the exhaust gas.
4. A system according to claim 3, wherein the system includes an NO-oxidation catalyst upstream of the filter, the catalyst being supported on a metal substrate of the type used in the filter, but at a lower packing density, to permit passage of soot particles.
5. A system according to any preceding claim, wherein the filter has, wholly or domain-wise, a regular coiled, woven or knitted structure.
6. A system according to any preceding claim, wherein the metal of the filter is Type 300 or Type 400 stainless steel.
7. A system according to any preceding claim, wherein the metal of the filter comprises an iron alloy containing at least 11.5% Cr, 4% Al and 0.02-0.25% minor constituents such as rare earth, zirconium or hafnium.
8. A system according to any preceding claim, wherein the width of the metal strip of the filter is up to 2, especially in the range of 0.1 to 0.5 mm and its thickness is 0.2 to 0.8 of its width.

9. A system according to claim 9, wherein the flat, narrow strip metal is a flattened wire
10. A system according to any preceding claim, wherein the filter packing carries a layer catalytic for soot oxidation.
11. A system according to claim 10, wherein the filter comprises a catalytic coating comprising a washcoat including Pt or oxides of Cs and V.
12. A system according to any preceding claim, comprising an exhaust gas treatment system comprising, in order from upstream to downstream, a plurality of metal-based filters adapted to successively trap smaller and smaller particles.
13. A system according to claim 12, comprising at least one wall flow filter for trapping yet smaller particles.
14. A system according to claim 12 or 13, comprising a flow-through monolith between the or each pair of metal-based filters.
15. A system according to claim 14, wherein the or each flow-through monolith comprises a NO oxidation catalyst, whereby to restore the NO₂ content, which had been decreased by reaction with soot in the preceding filter.
16. A system according to any preceding claim, wherein the filter capacity is sufficient to allow the soot to be combusted continuously by the oxidant.
17. A system according to any of claims 1 to 16, wherein the filter capacity is sized for accumulations of soot sufficient to increase pressure-drop significantly before the next period of fast running and the system includes a bypass the pressure-drop through which is equal to the design maximum tolerated pressure-drop through the filter(s) whereby to avoid engine stalling.

18. A system according to claim 17, comprising means to limit soot emission to atmosphere, which means comprising a second stage such as a filter or impingement collector and/or an oxidation catalyst downstream of the bypass.
19. An internal combustion engine comprising an exhaust system according to any preceding claim.
20. A diesel engine according to claim 19.
21. A method of treating an exhaust gas of an internal combustion engine, which method comprising the steps of trapping soot in the exhaust gas on a filter, generating an oxidant more active than molecular oxygen (O₂) for combusting soot collected on the filter from exhaust gas components and combusting the trapped soot in the oxidant, wherein the filter comprises a mass of elongate flat, narrow strip metal.

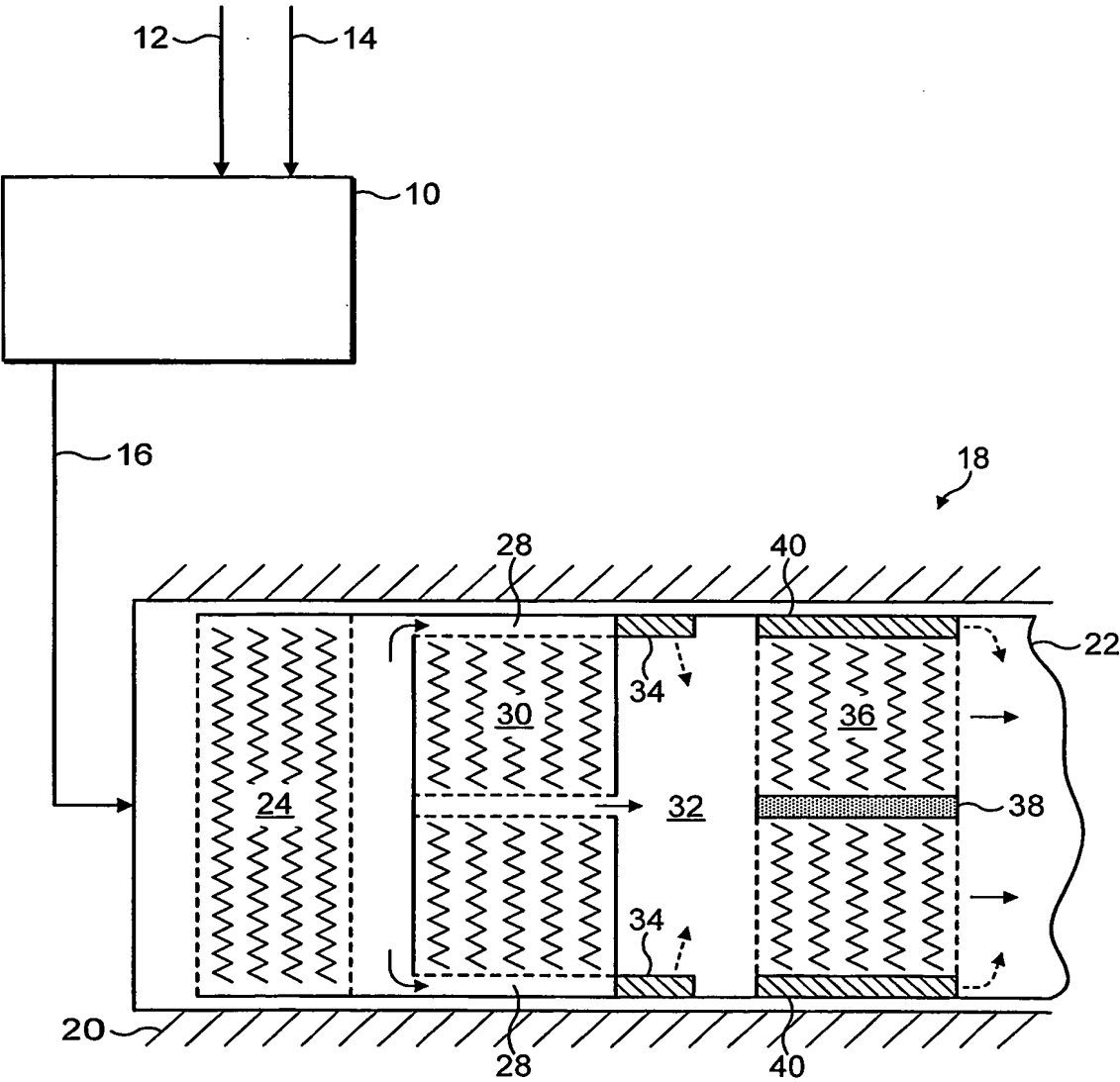


FIG. 1

Figure 2

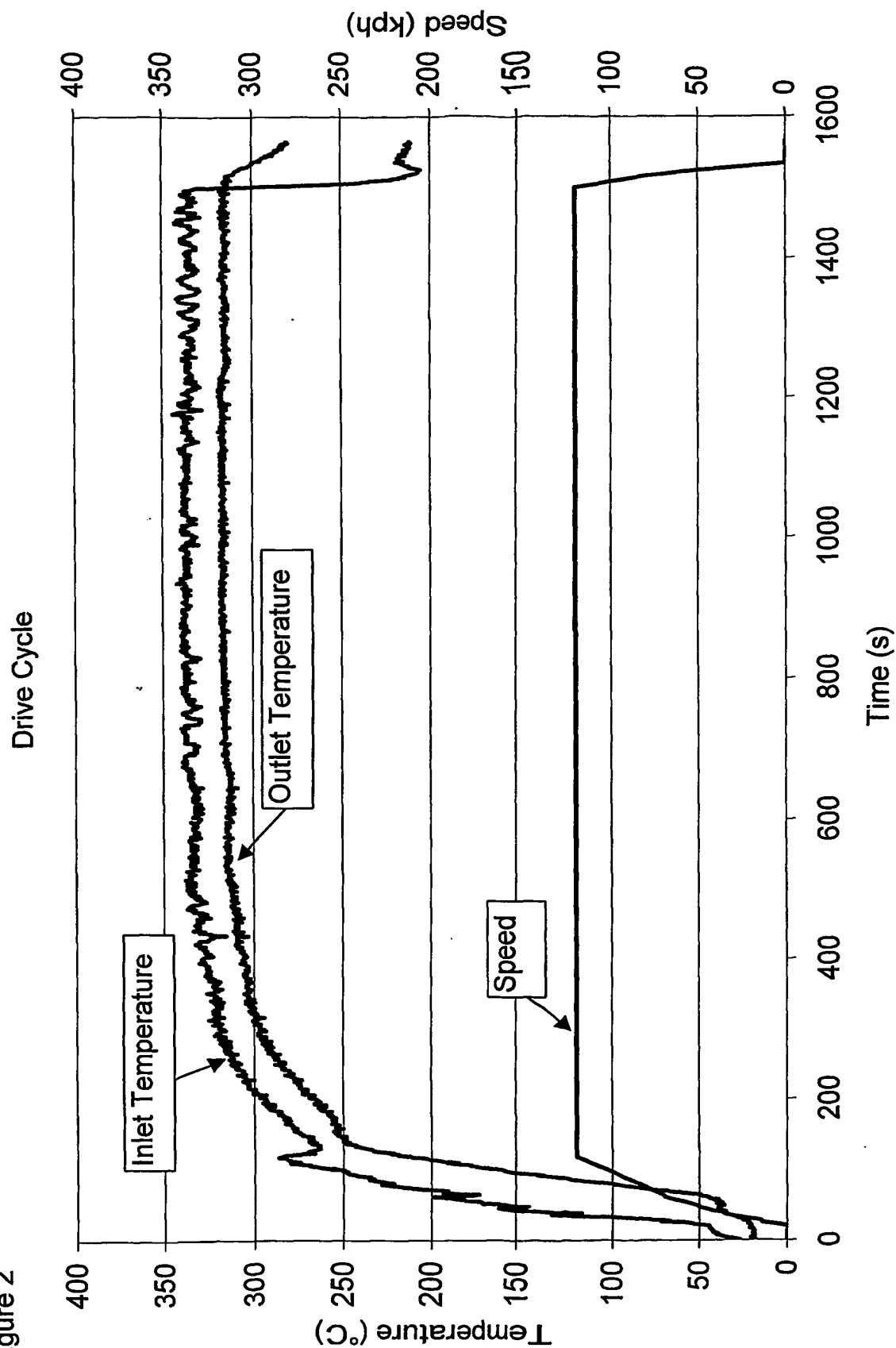


Figure 3

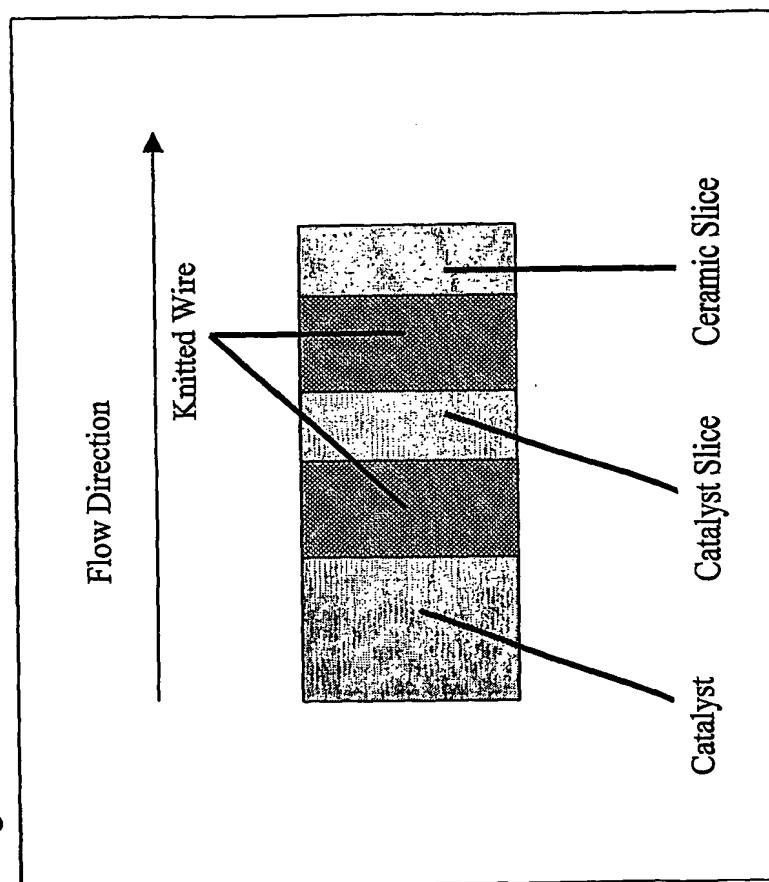


Figure 4

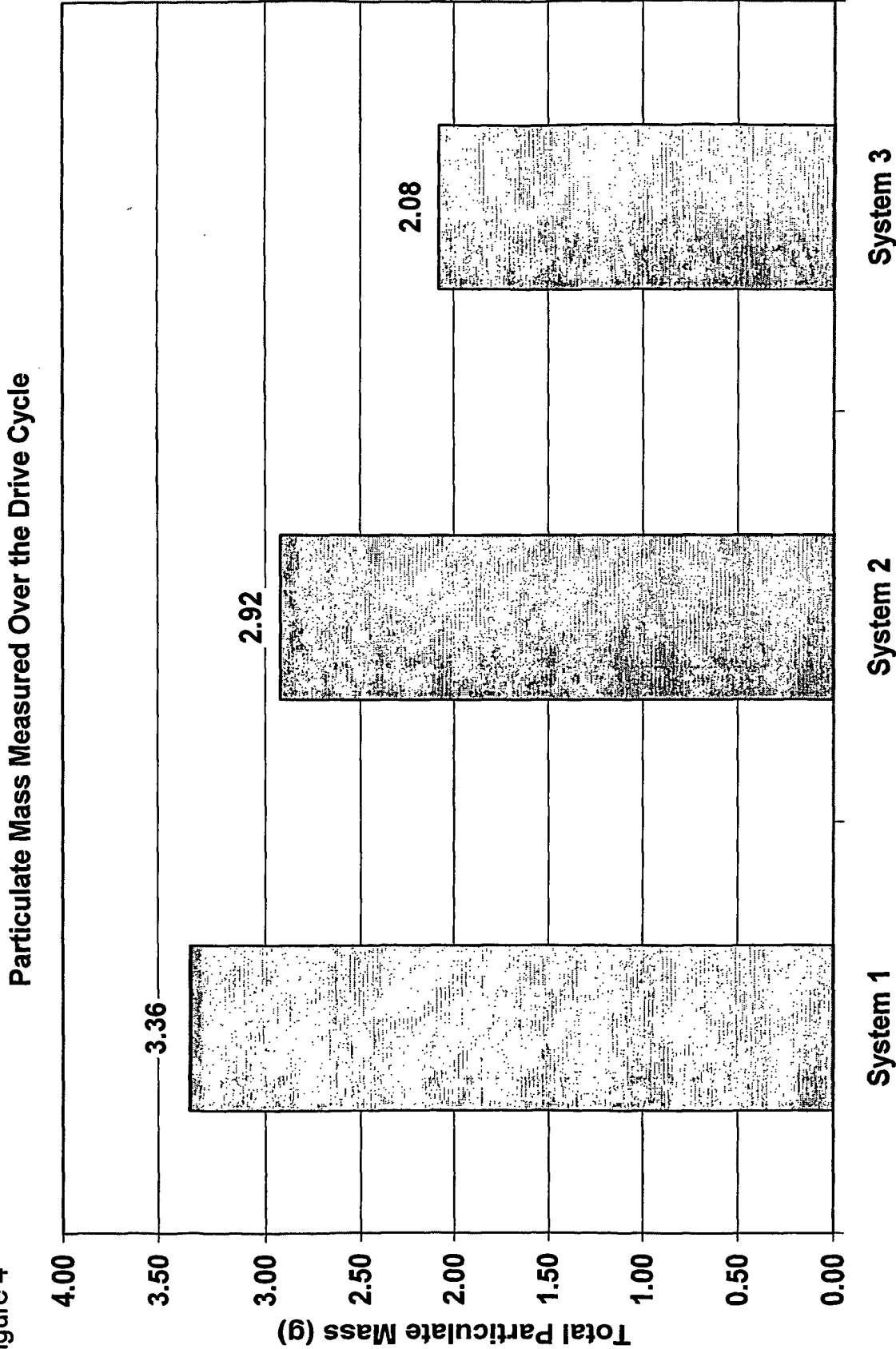
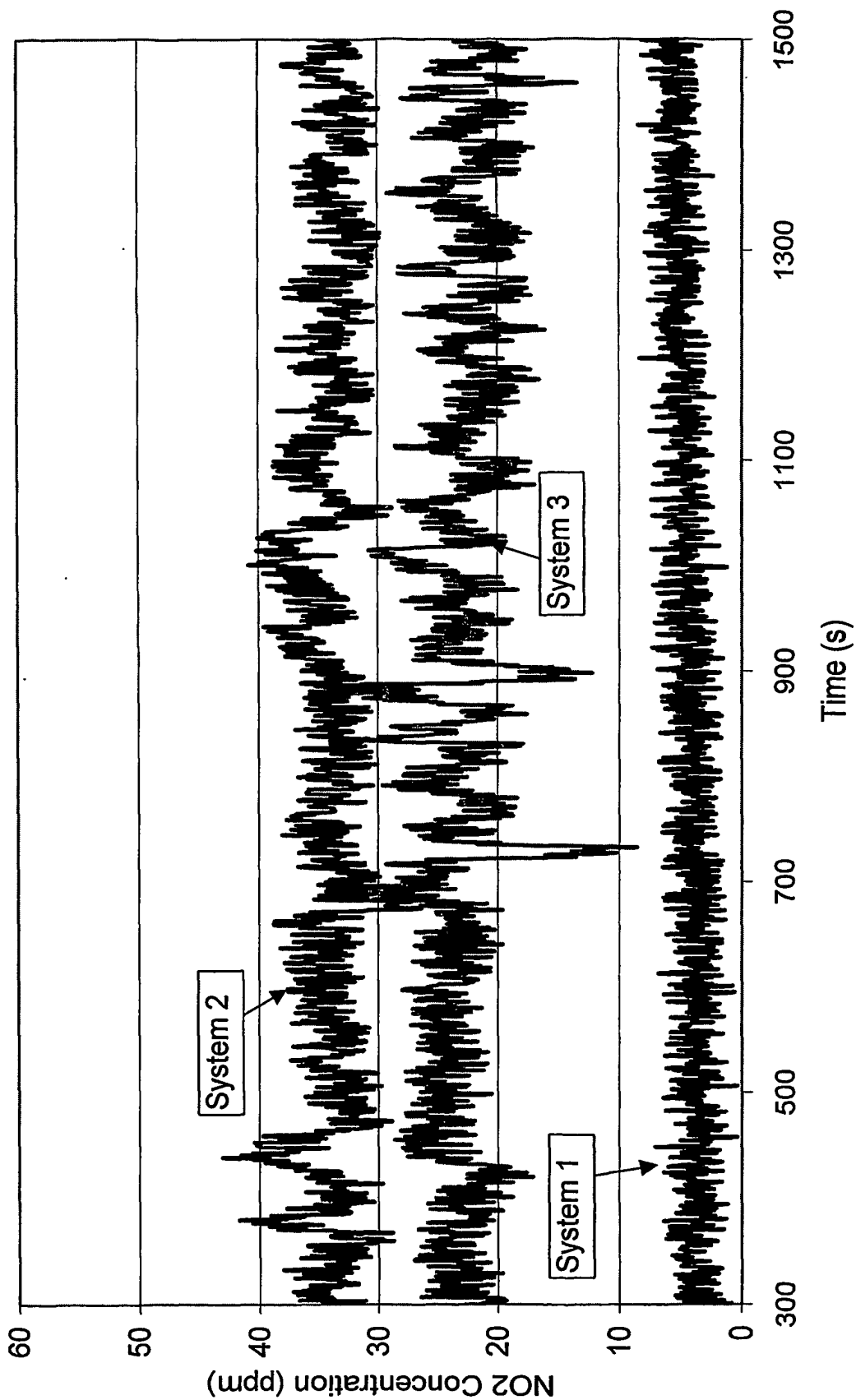


Figure 5 NO₂ Concentration (ppm) at the Tailpipe Measured Over the Drive Cycle



INTERNATIONAL SEARCH REPORT

PCT/GB 03/03462

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 F01N3/023 F01N3/022 F01N3/08 F01N3/031 F01N3/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 F01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 99 44725 A (JOHNSON MATTHEY PLC ;CHANDLER GUY RICHARD (GB); TWIGG MARTYN VINCE) 10 September 1999 (1999-09-10) page 1, line 6 -page 6, line 26; figures 1-4	1-5, 7-9, 17-21
Y	EP 0 061 304 A (JOHNSON MATTHEY PLC) 29 September 1982 (1982-09-29) page 6, line 7 -page 7, line 9 page 15, line 7 - line 15; figure 3	1-5, 7-9, 17-21
E	EP 1 262 641 A (MITSUI BUSSAN) 4 December 2002 (2002-12-04) paragraph '0053! - paragraph '0062! paragraph '0097! - paragraph '0099!; figure 3	1-5, 10-21

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

31 October 2003

Date of mailing of the international search report

07/11/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Nobre, S

INTERNATIONAL SEARCH REPORT

PCT/GB 03/03462

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 01 96717 A (CHAPMAN KENNETH HAZEL ;JOHNSON MATTHEY PLC (GB); WILKINS ANTHONY J) 20 December 2001 (2001-12-20) page 2, line 5 -page 12, line 3; figure 1 -----	1-5,7, 10,11,21
A	US 4 902 487 A (JUNG HYUN J ET AL) 20 February 1990 (1990-02-20) page 1, line 9 -page 4, line 13; figure 1 -----	1-5,10, 11,21

INTERNATIONAL SEARCH REPORT

PCT/GB 03/03462

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9944725	A	10-09-1999	AT 221797 T CA 2323359 A1 DE 69902446 D1 DE 69902446 T2 DK 1060004 T3 EP 1060004 A1 WO 9944725 A1 JP 2002505402 T	15-08-2002 10-09-1999 12-09-2002 24-04-2003 02-12-2002 20-12-2000 10-09-1999 19-02-2002
EP 0061304	A	29-09-1982	EP 0061304 A1 CA 1185589 A1 EP 0053884 A1 JP 57165041 A US 4464482 A	29-09-1982 16-04-1985 16-06-1982 09-10-1982 07-08-1984
EP 1262641	A	04-12-2002	JP 2002336627 A EP 1262641 A1 ZA 200203741 A	26-11-2002 04-12-2002 15-11-2002
WO 0196717	A	20-12-2001	EP 1290318 A1 WO 0196717 A1 US 2003180195 A1	12-03-2003 20-12-2001 25-09-2003
US 4902487	A	20-02-1990	AT 132940 T DE 68925382 D1 DE 68925382 T2 DK 233389 A EP 0341832 A2 ES 2081301 T3 GR 3018800 T3 IE 71167 B1 JP 1318715 A JP 3012249 B2 NO 891936 A ,B,	15-01-1996 22-02-1996 15-05-1996 14-11-1989 15-11-1989 01-03-1996 30-04-1996 29-01-1997 25-12-1989 21-02-2000 14-11-1989